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Attestation

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**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

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Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

Electronic component comprising an electrically conductive relief structure and a method of manufacturing a relief structure on an electrically isolating substrate

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Electronic component comprising an electrically conductive relief structure and a method of manufacturing a relief structure on an electrically isolating substrate.

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The invention relates to [preamble claim 1].

The invention further relates to [preamble claim 9].

5 Such a component and such a method are known from US-A- 5,561,030. The relief structure of the component consists of a number of tracks and is placed on a planar substrate. The salts of poly(substituted thiophenes) known for use as track material are salts of poly-3-alkylthiophenes, of poly-3-alkoxythiophenes and of poly-3,4-dialkoxythiophenes. In the known method the tracks of the relief structure are used as interconnects and as resistors.

10 In the known method a poly(substituted thiophene) is applied as a layer on a substrate. After irradiating the layer, the unirradiated areas of the applied layer are removed by washing, leaving tracks behind and forming a relief structure. The salt of the poly(substituted thiophene) is formed by oxidation with an iron- or a gold salt after the washing step, thereby making the relief structure electrically conductive.

15 The known component has, however, disadvantages: a first disadvantage is that the conductivity of the tracks in the relief structure deteriorates within a day, except when using a gold salt as the oxidant. This oxidant is, however, expensive. So, either the component is not stable enough for commercial use, or the costs of its manufacture are high. A second disadvantage is that the tracks are as wide as 1 mm, except if the complicated technique of

20 laser lithography is used. The track length and the distance between tracks is not mentioned, but will be in the same order of magnitude. A component with such dimensions has a size too large for applications in identification tags. Their production is too expensive as well, as the production costs of a component are inversely related to the number of components in a production batch.

25

It is an object of the present invention, inter alia, to provide a component of the kind described in the opening paragraph, which has a stable conductivity. It is a further object

to provide a method of the kind mentioned in the opening paragraph, which allows the manufacture of small tracks with a stable conductivity at low costs.

The object to provide an electronic component is achieved by a component as specified in the opening paragraph, characterized in that:

5 the relief structure contains a salt of a poly-3,4-alkylenedioxythiophene, in which the alkylene group is chosen from the group consisting of an optionally C_1 to C_{12} -alkyl- or phenyl-substituted methylene group, an optionally C_1 to C_{12} -alkyl- or phenyl substituted 1,2-ethylene group, a 1,3-propylene group and a 1,2-cyclohexylene group and

the relief structure comprises at least one electrode.

10 The stable conductivity of the component aimed at is achieved due to the choice of an electrically conductive salt of a specific group of poly(3,4-substituted thiophenes), hereinafter also called PEDOTs. The optional alkyl substitution is limited to an C_1 to C_{12} -alkyl group, as a larger alkyl group reduces the processability of the PEDOT too much. The structure containing a PEDOT salt may comprise interconnects and resistors, apart from one or
15 more electrodes. The electrodes can for example be part of a diode, a bipolar transistor or a field effect transistor. A clear advantage of a component with an electrically conductive relief structure comprising a salt of a PEDOT is the excellent stability of the relief structure and of the material on bringing the structure in contact with, for instance, organic and aqueous solvents, polymeric melts or deposited vapors. Contrary to relief structures containing
20 polyaniline, relief structures containing a PEDOT salt are neither subject to dissolution nor to deterioration of their conductivity in basic solutions.

A layer on a substrate surface, which comprises a pattern of an electrically conductive PEDOT, is known from US-A 5,447,824. This layer comprises conductive areas and less conductive areas. However, leakage currents taking place through the less conductive
25 areas obstruct the use of the conductive areas as electrodes.

The component with an electrically conductive relief structure of a salt of PEDOT can be realized using e.g. state-of-the-art printing techniques such as inkjet or silkscreen printing. Lithographic techniques can alternatively be used, especially for the manufacture of tracks with relatively small track widths and relatively small distances between
30 tracks.

In an embodiment of the component of the invention, the relief structure comprises neighboring tracks at a distance of less than 10 μm . Such neighboring tracks can for example be used as leads carrying input or output signals or as electrodes. In a field effect transistor such tracks can function as a pair of a source and a drain electrode. If the area

between the electrodes is filled with semiconductor material, the area functions as a channel. The distance between the neighboring tracks defines the channel length cL . As known from Brown et.al., *Synthetic Metals* 88(1997), 37-55, a small channel length leads to a large source-drain current and a high on-off ratio in the transistor.

5 In a preferred embodiment of the component of the invention, the neighboring tracks are able to function as a pair of a source and a drain electrode. At least one of the tracks is fork shaped having more than one prong, while the electrodes are interdigitated. These electrodes are positioned so as to enlarge the area of mutual exposure. This embodiment enlarges the source-drain current at a chosen drain voltage and thereby the on/off ratio.

10 In another embodiment of the electronic component of the invention, the component comprises, separated from the said – first - relief structure at least by an insulating layer, a second relief structure of an electrically conductive material. The second relief structure prevents leakage currents between tracks in use as interconnects and between tracks in use as electrodes in different transistors, diodes and capacitors.

15 In a preferred embodiment the second relief structure also comprises a salt of a PEDOT.

In a further embodiment, the component of the invention comprises a field-effect transistor. Such a transistor contains a source and a drain electrode, which are interconnected through a channel comprising a semiconducting material. It further comprises a
20 gate electrode, which is separated from the source and the drain electrode by at least an insulating layer. In this embodiment one relief structure of the component contains the source and the drain electrode. Preferably these electrodes interdigitate in order to enlarge the channel width. Another relief structure contains the gate electrode. At least one of said relief structures is the relief structure comprising a salt of a PEDOT. The other, second electrically conductive
25 relief structure comprises a salt of a PEDOT, a polyaniline, silicium or a metal such as gold. As is known in the art of transistor fabrication, different designs are possible, such as a 'top-gate'-design and a 'bottom-gate'-design.

In another embodiment of the component of the invention, the salt of the PEDOT is a polyacid salt. Poly(styrene-sulphonic acid) is used as the polyacid by preference.

30 In a further embodiment, not only the first relief structure, but the complete component substantially consists of polymeric material. Such an "all-polymeric" device has favorable properties, such as a high mechanical flexibility and a low weight. Besides, the component is cheap and hazardous substances may easily be avoided during its manufacture.

Polymeric materials for the semiconductor layer are known from WO-A 99/10939. Examples include polypyrroles, polyphenylenes, polythiophenes, polyphenylene-vinylenes, polythienylene-vinylenes, poly(di)acetylenes, polyfuranes, polyfuranylenes-vinylenes and polyanilines. Alternatively, substituted derivatives of these polymers are applied. Examples of substituents are alkyl- and alkoxy-groups and ring-shaped groups, such as alkylenedioxy-groups. By preference, the substituent groups have a carbon chain of 1 to 10 carbon atoms. As known by those skilled in the art, such materials may be rendered semiconducting by doping with e.g. an oxidizing agent, a reducing agent and/or an acid. A preferred choice is polythienylene-vinylene.

10 Polymeric materials for the insulating layer are known from US-A- 5,347,144. Examples include polyvinylphenol, polyvinyl alcohol and cyanoethylpullane. Preferably an insulating material with a dielectric constant of at least six is used, such as polyvinylphenol, which can be rendered insoluble by cross-linking with a cross-linking agent such as hexamethoxymethylenemelamine and heating.

15 Substrate materials are e.g. polymers as for instance polystyrene, polyimide, polyamide and polyester, or glass, ceramics or silica.

The object relating to the method is achieved in that [the characterizing portion of claim 9].

20 The object relating to the method contains three elements: the manufacture of tracks with stable conductivity, the manufacture of components with small tracks and manufacturing at low costs. The stable conductivity is realized in that the composition used in the method according to the invention comprises a salt of a PEDOT. Such a composition is commercially available, but it was not known to be applicable in the manufacturing of electrically conductive relief structures. US-A 5,300,575 teaches the use of this composition to provide an anti static layer only.

25 The small tracks can be achieved by the use of a salt of a PEDOT containing a polyacid anion as counterion, hereinafter also referred to as a polyacid salt. This polyacid salt substantially enhances the processability of the PEDOT. As a polyacid is soluble in polar solvents such as water, the polyacid salt of the PEDOT is also more or less soluble in water or at least miscible with water. By irradiating a layer of a polyacid salt of PEDOT with UV-
30 radiation according to a desired pattern and subsequently re-dissolving the salt, relief structures with track widths and channel lengths of 10 μm can be achieved. In the art of plastic electronics such tracks may be called small.

The manufacturing at low costs is realized in that it is not necessary to use resist layers and that water can be used as a solvent.

Examples of polyacids include poly(styrene sulphonic acid), polyacrylic acid, polymethacrylic acid, poly(vinyl sulphonic acid), poly(vinyl sulphuric acid), poly(vinyl boric acid), poly(styrene boric acid), poly(vinyl phosphoric acid), and poly(styrene phosphoric acid).

In the method of the invention the radiation-sensitive layer can be applied on a substrate by spincoating, webcoating or electrical deposition of a solution or dispersion and subsequently removing the solvent or dispersion agent. For the irradiation use can be made of UV-radiation and a photomask, or of laser light, electron, X-ray or ion beams. Irradiation influences the initiator present, such as the azide 4,4'-diazidobenzalactone-2,2'-disulphonic acid disodium salt. This initiator is assumed to initiate cross-linking between polymeric molecules present in the radiation-sensitive layer. The removal of the unirradiated areas during the washing can be enhanced in a spray process.

In a preferred embodiment of the method of the invention, the composition comprising the polyacid salt of the PEDOT is filtrated before application on the substrate. Preferably, a filter having pores with a diameter of 5 μm or less is used in the filtration. The filtration prevents the eventual presence of particles larger than the widths of the tracks formed.

The invention will be explained by means of exemplary embodiments and the accompanying drawings, wherein:

Fig. 1 shows the structural formulae of the repeating units of a poly-3,4-alkylenedioxythiophene, with alkylene groups ethylene (I-1), 1,2-cyclohexylene (I-2), phenylethylene (I-3), propylethylene (I-4), methylene (I-5) and 1,3-propylene (I-6);

Fig. 2 shows the structural formula of a polyanion salt of poly-3,4-ethylenedioxythiophene, with $n, m > 10$;

Fig. 3 schematically shows a plan view of a field-effect transistor containing conductive relief structures of the component according to the invention;

Fig. 4 schematically shows a cross-sectional view of a field-effect transistor with two relief patterned conductive layers, in which the first layer comprises the source and the drain electrode and in which the second layer contains the gate electrode;

Fig. 5 schematically shows a plan view of field-effect transistor with interdigitated source and a drain electrodes. For reasons of clarity the substrate, the insulating layer and the semiconductor layer are omitted from the drawing.

5

Embodiment 1

The structural formula of the poly(styrene sulphonic acid) salt of poly-3,4-ethylenedioxythiophene is shown in figure 2. A composition of this salt in water is commercially available from Bayer. The concentration of PEDOT in this composition is 0.5 weight per cent and that of polystyrene sulphonic acid is 0.8 weight per cent. To the composition, apparently a colloidal solution, 0.15 weight per cent of the initiator 4,4'-diazidobenzalactone-2,2'-disulphonic acid disodium salt was added. After filtration through a 5 μm filter, the composition was spincoated on an isolating and planarized substrate. The layer obtained was dried at 30°C for 5 minutes. The dried layer was exposed, via a mask to patterned radiation with UV light ($\lambda = 360\text{ nm}$), by means of a Hg lamp. The layer was washed by spraying with water. In this washing the unirradiated areas of the layer were dissolved. After drying, the average layer thickness of the remaining areas was 80 nm. These areas had a specific electric conductivity of 1 S/cm. Each continuous undissolved area functions as a track, having track widths of 5, 8, 10 or 20 μm . Distances between the tracks were 8, 10 or 20 μm .

Embodiment 2

3,4-Ethylenedioxythiophene, an Fe(III)-salt such as tris(toluenesulphonate)Fe(III) and a base such as imidazole were dissolved in butanol. The solution was put in an inkjet printer. A structure was printed according to a desired pattern on an electrically insulating surface. The obtained relief structure was first dried and subsequently heated to 110°C in order to polymerize the ethylenedioxythiophene. It was then washed so as to remove the iron salts, the base and the not-polymerized 3,4-ethylenedioxythiophene. The resulting electrically conducting relief structure comprises a salt of poly-3,4-ethylenedioxythiophene (I-1) and toluenesulphonic acid. The track width in the relief structure is about 50 μm .

Embodiment 3

Fig. 3 schematically shows a plan view of a field-effect transistor 1 containing conductive relief structures of the component according to the invention. Fig. 4 schematically shows (not drawn to scale) the field-effect transistor 1 in a cross-sectional view taken on the line I-I in Fig.3. The field-effect transistor 1 comprises an electrically insulating substrate 2, on which is provided a first electrically conductive, relief structure 3 of a polymeric material. This relief structure 3 comprises a source electrode 34 and a drain electrode 35 with a track width tW . On the first relief structure a semiconductor layer 4 is provided, which layer 4 comprises a channel 41 with channel length cL and channel width cW . Covering the layer 4 and thus the channel 41 is an electrically insulating layer 5. It electrically insulates the gate electrode 64 from the channel 41, said gate electrode 64 being accommodated by the second electrically conductive relief structure 6. The transistor 1 is of the "top gate" type.

Embodiment 4

Fig. 5 schematically shows a plan view of field-effect transistor 11, which comprises a first relief structure 3 accommodating an interdigitated pair of a source electrode 31 and a drain electrode 32. For reasons of clarity the substrate, the insulating layer and the semiconductor layer are omitted from the drawing. The source electrode 31 is fork-shaped and comprises parallel tracks 311, 312, 313 and 314. The drain electrode 32 is fork-shaped and comprises tracks 321, 322, 323 and 324. In this example each of the electrodes 31, 32 comprises four tracks with a track width tW , which is however neither necessary nor meant to be limiting. The source 31 and drain electrode 32 are separated by a channel 141 with a channel length cL . The transistor 11 further comprises a second relief structure comprising electrical conductors 611 and a gate electrode 61. The transistor 11 is of a "bottom gate" type.

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CLAIMS:

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1. An electronic component comprising an electrically conductive relief structure (3) on a surface of an electrically insulating substrate (2), which structure comprises a salt of a poly(3,4-substituted thiophene) as electrically conductive material, characterized in that:

- 5 – the relief structure (3) contains a salt of a poly-3,4-alkylenedioxythiophene, in which the alkylene group is chosen from the group consisting of an optionally C₁ to C₁₂- alkyl- or phenyl substituted methylene group, an optionally C₁ to C₁₂-alkyl- or phenyl substituted 1,2-ethylene group, a 1,3-propylene group and a 1,2-cyclohexylene group and
- the relief structure (3) comprises at least one electrode (32).

10

2. An electronic component as claimed in Claim 1, characterized in that the relief structure (3) comprises neighboring tracks (341, 351) at a distance of less than 10 µm.

15

3. An electronic component as claimed in Claim 2, characterized in that neighboring tracks (341, 351) form a pair of a source and a drain electrode (34, 35), at least one of which being fork-shaped, the source and the drain electrode being interdigitated.

20

4. An electronic component as claimed in Claim 1 or 2, characterized in that the component comprises, separated from the said relief structure (3) at least by an insulating layer (5), a second electrically conductive relief structure (6).

5. An electronic component as claimed in Claim 4,

25

characterized in that the second relief structure (6) contains a salt of a poly-3,4-alkylenedioxythiophene, in which the alkylene group is chosen from the group consisting of an optionally C₁ to C₁₂- alkyl- or phenyl substituted methylene group, an optionally C₁ to C₁₂-alkyl- or phenyl substituted 1,2-ethylene group, a 1,3-propylene group and a 1,2-cyclohexylene group.

6. An electronic component as claimed in Claim 4, characterized in that the component comprises a field-effect transistor (1).

7. An electronic component as claimed in Claim 1,

5 characterized in that said salt of poly-3,4-alkylenedioxythiophene contains a polyacid anion as counterion.

8. An electronic component as claimed in Claim 1, characterized in that the component substantially consists of organic polymeric material.

10

9. A method of manufacturing a relief structure (3) on a electrically insulating substrate (2), the relief structure (3) comprising an electrically conductive polymeric material, which method comprises:

15

- applying a radiation-sensitive composition on the substrate to form a layer, which composition contains a poly(3,4-substituted thiophene) and
- irradiating said layer according to a desired pattern, thereby obtaining irradiated, cross-linked areas and unirradiated areas,

characterized in that:

20

- a radiation-sensitive composition is used which contains a salt of a poly-3,4-alkylenedioxythiophene as electrically conductive polymeric material, in which the alkylene group is chosen from the group consisting of an optionally C₁ to C₁₂- alkyl- or phenyl substituted methylene group, an optionally C₁ to C₁₂-alkyl- or phenyl substituted 1,2-ethylene group, a 1,3-propylene group and a 1,2-cyclohexylene group;

25

- said salt of poly-3,4-alkylenedioxythiophene contains an anion of a polyacid as its anion and
- the unirradiated areas are removed by washing to form the electrically conductive relief structure thereby.

10. A method as claimed in Claim 9,

30

characterized that the composition prior to being applied on the substrate is filtrated through a filter having pores with a diameter of at most 5 µm.

ABSTRACT:

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An electronic component has an electrically conductive relief structure (3), which contains a salt of a poly-3,4-alkylenedioxythiophene. This salt provides the structure with a stable conductivity. The salt is a polyacid salt by preference. In the method of manufacturing a relief structure on an electrically insulating substrate the polyacid salt of poly-3,4-alkylenedioxythiophene is used. Relief structures (3) comprising tracks (311-314, 321-324) and channels (141) with track widths (tW) and channel lengths (cL) of less than 10 μm can be achieved. The tracks (311-314; 321-324) are used as electrodes (31;32), the channels (141) are used as semiconductor channels in electronic components, especially in field-effect transistors (11).

10

Fig.5

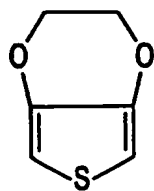
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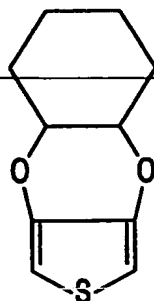
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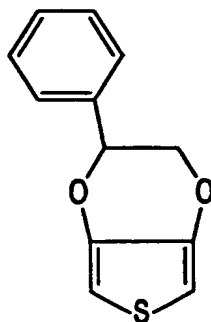
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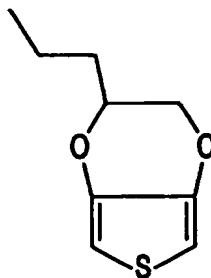
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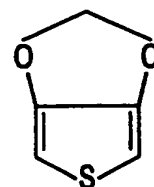
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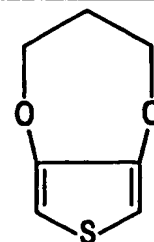
I-3



I-4



I-5



I-6

FIG. 1

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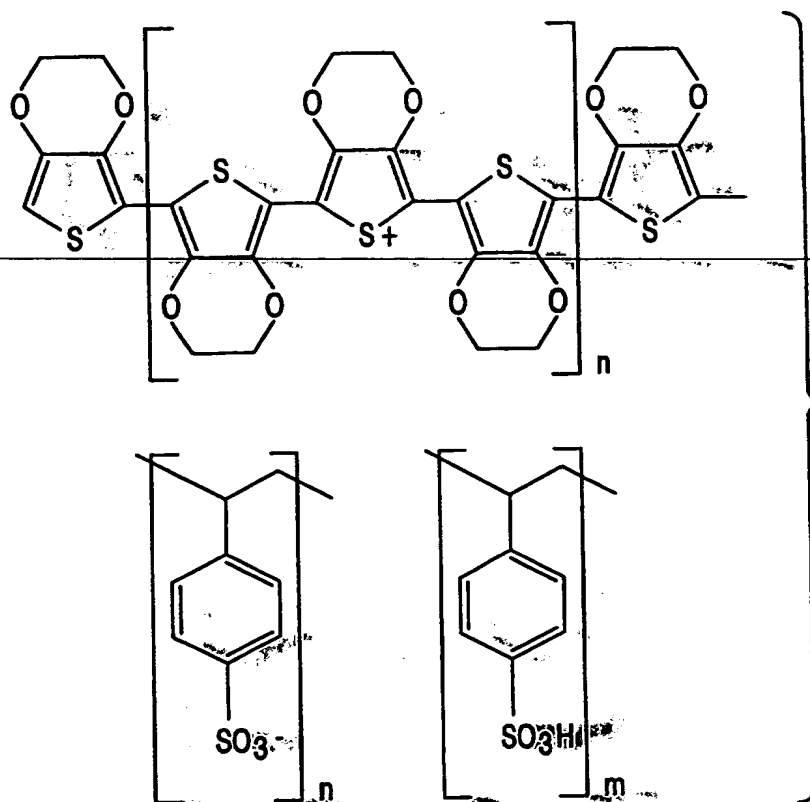


FIG. 2

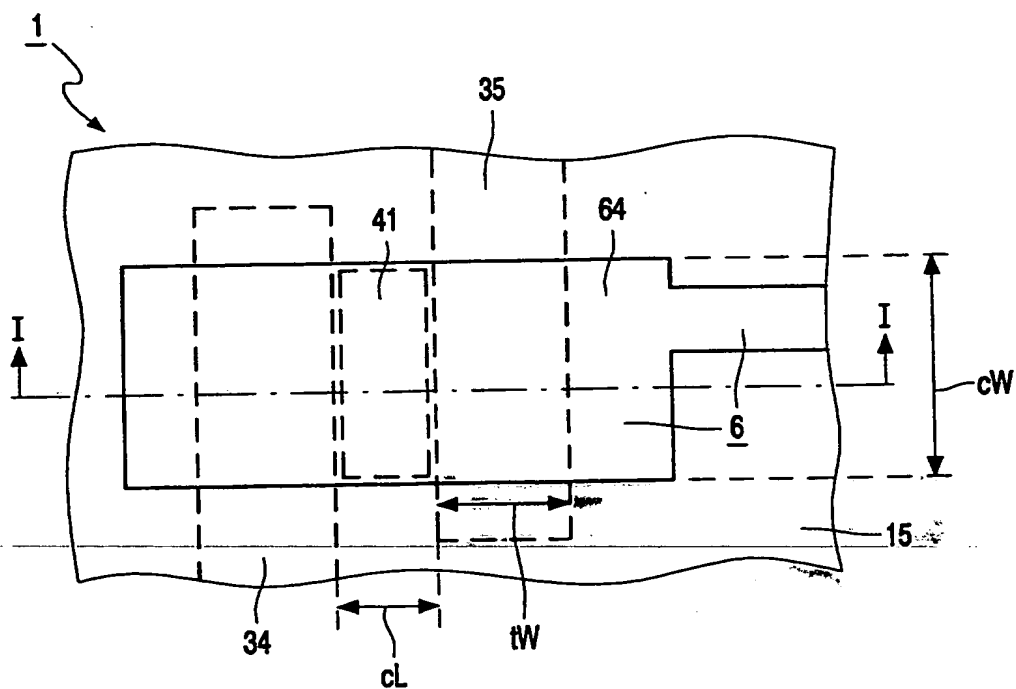


FIG. 3

A cross-sectional view of a semiconductor device 11. The device features a substrate 3 with a central region 31. Within this region, there are multiple layers: a bottom layer 32, followed by a stack of layers 321, 322, 323, and 324. A top layer 314 is positioned above the stack. A central vertical structure 611 is located within the central region 31. The device is enclosed in a frame 61, which has a top portion 611. A dashed line 11 indicates the overall structure. Other labels include 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 92



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